Update to the LUSTOP "Guide to Satisfying Regulatory Requirements and Protecting Groundwater"

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Leaking Underground Storage Tank Oversight Program

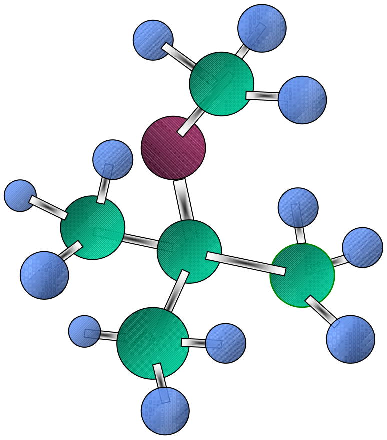
MTBE and Other Recalcitrant Petroleum Constituent Releases from USTs

The intent of this update is to provide general information regarding cleanup of recalcitrant compounds released from USTs.

SANTA CLARA VALLEY WATER DISTRICT

What is a recalcitrant chemical?

A recalcitrant chemical is one that does not undergo significant natural attenuation processes in the subsurface. In addition, if the chemical moves quickly (is highly mobile) in the subsurface, it can contaminate large volumes of water and is more difficult to investigate and clean up. Chemicals used in gasoline, such as methyl tert butyl ether (MTBE), other ether oxygenates, and 1-2 dichloroethane tend to be both mobile and recalcitrant. Chemicals such as ethylene dibromide (EDB), tend to be recalcitrant, although they are not highly mobile. The most commonly detected and pervasive recalcitrant and mobile chemical found in groundwater in Santa Clara County is MTBE. MTBE is a synthetic organic ether that has been added to gasoline as early as 1979. It was originally added as an octane enhancer following the phase out of lead. Since 1990, it has been blended into gasoline as a result of Federal and State clean air requirements. Other oxygenates blended into gasoline as a result of clean air requirements include tert-amyl methyl ether (TAME), ethyl tert-butyl ether (ETBE), di-isopropyl ether (DIPE) and tert-butyl alcohol (TBA).



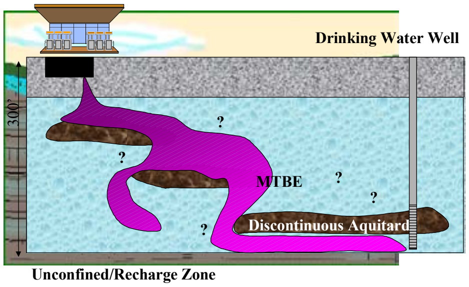
methyl tert-butyl ether
(MTBE)

A recalcitrant chemical, such as MTBE, does not readily degrade once released to the subsurface.

Why the concern about ether oxygenates such as MTBE?

In the City of Santa Monica, MTBE contamination prompted officials to shut down half of the City's drinking water supply wells, causing greater dependence on more expensive imported water. In South Lake Tahoe, MTBE pollution in groundwater has led to the shut down of many City wells, and resulting in mandated water conservation measures. In Santa Clara County, MTBE has been detected at low levels in several drinking water supply wells.

Approximately half of the drinking water in Santa Clara County comes from groundwater supplies. Continued degradation of groundwater quality, particularly in drought years, could challenge the District's ability to provide a sufficient quantity of high quality water. **Therefore, the District is undertaking a significant effort to protect groundwater basins from MTBE contamination by ensuring that MTBE releases to groundwater are properly investigated and cleaned up.** In July 1997, the District began requiring detailed investigation and cleanup of MTBE affected fuel leak sites.


Significant Dissolved Contaminant Mass Near Source
Low Level Plume Potentially Impacting Drinking Water Supply

Why is a new cleanup approach needed for MTBE?

- MTBE's chemical characteristics make it a more significant threat to groundwater resources than most other petroleum compounds in gasoline (benzene, toluene, etc.). MTBE has a low adsorption potential (less likely to adhere to soil) and high solubility in water (dissolves more readily in water) making MTBE highly mobile. In addition, its apparent lack of biodegradation (not readily broken down by microbes) make it recalcitrant (persistent) in the subsurface.

MTBE is a common example of a recalcitrant chemical which is affecting drinking water supplies across the State.

- Results of detailed soil and water investigations at MTBE sites within Santa Clara County have shown that MTBE plumes tend to be larger than those of most other petroleum constituents.

- Determining the fate and transport (how and where a chemical moves) of MTBE at a site can be very complex. Factors such as fast groundwater flow rates, changing groundwater flow directions, and variable soil types, along with MTBE's chemical characteristics, make investigation and cleanup of MTBE contamination more complex. Because of to the complexity of MTBE plumes, a detailed investigation to locate the plume must be conducted before final cleanup strategies are implemented. However, interim cleanup is needed to reduce mass and control movement of many of these plumes. Often, interim cleanup can be initiated while the soil and water investigation is being completed.

- MTBE has been detected in groundwater at more than 70% of gasoline UST leak sites in Santa Clara County, a trend that is observed across the State.

  Due to MTBE's prevalence in groundwater, its potential to migrate long distances, and increasing detections in drinking water supplies, the District has determined that interim cleanup will be necessary at many sites to stop the movement of MTBE plumes and prevent further contamination of drinking water supply wells.

MTBE movement in the subsurface can be complex and constitutes a bigger threat to drinking water than most other hydrocarbons.

Which sites will be requested to perform interim cleanup?

Because of the properties of MTBE and its behavior in groundwater, interim remediation and/or final cleanup will be required at many sites. In general, most sites will be directed to perform detailed investigations. The results of detailed soil and water investigations, hydrogeologic studies, and conduit studies will determine the urgency and necessity of interim cleanup and the selection of cleanup strategies. Source characterization and interim remedial actions may be required at sites with a small quantity of MTBE mass or several hundred parts per billion (ppb) of dissolved MTBE in groundwater. For instance, at sites where limited data is available (unknown source area concentrations, limited information regarding the nature of the release, or undefined extent of contamination) a screening concentration for MTBE of 200 ppb[1] will be used by the District to request further investigation and submittal of a work plan for interim cleanup. However, all sites will be reviewed and requests will be made based on the information available. Since each site is different, other factors and/or data obtained from further investigation may be used for determining site specific cleanup actions.

The results of detailed investigations help determine the urgency of cleanup and selection of effective cleanup technologies.

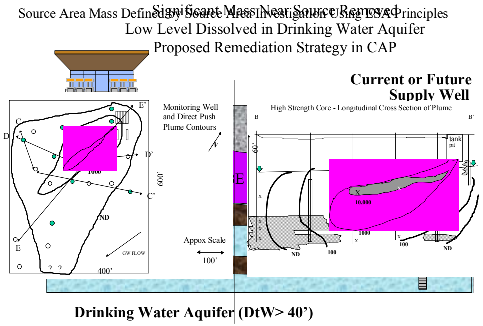

Source Area Mass Defined By Source Area Investigation Using ESA Principles
Significant Mass Near Source Removed
Low Level Dissolved in Drinking Water Aquifer
Proposed Remediation Strategy in CAP
Current or Future Supply Well
Monitoring Well and Direct Push Plume Contours
High Strength Core - Longitudinal Cross Section of Plume
B
B'
C
C'
D
D'
E
E'
1000
ND
600'
400'
GW FLOW
Appox Scale
100'
60'
tank pit
10,000
1000
100
ND
Drinking Water Aquifer (DtW> 40')

Figure 2

How do detailed investigations and the use of ESA principles assist in interim cleanup decisions?

The use of an expedited site assessment (ESA) approach to the soil and water investigation provides detailed, three-dimensional definition of the plume and transport pathways. ESA begins with development of a conceptual model for the release and resulting plume to assist in selecting sampling locations. Tools such as soil-gas surveys, direct push technologies to collect depth discrete soil and water samples, field screening tools, and in some cases on-site labs can be useful for faster and more cost effective site investigation. Detailed investigations can identify discrete areas of high concentrations of MTBE. Interim cleanup can focus on the most contaminated areas while plume characterization is occurring.

How are cleanup levels determined?

Development of interim cleanup levels can vary by site and are dependent on the risks present at the site and the cost effectiveness of the interim cleanup strategy.

Final cleanup levels for the site are proposed in the Corrective Action Plan (CAP) prepared after completion of the soil and water investigation. The cleanup levels proposed in the CAP shall comply with the requirements of Section 2721 (b) of Chapter 16, Division 3, California Code of Regulations (CCR) Title 23 and meet the numerical objectives established in the San Francisco Bay or Central Coast Regional Water Quality Control Plan (please refer to page 8 of "Guide to Satisfying Regulatory Requirements and Protecting Groundwater" for additional information regarding corrective action plans). The water quality control plans designate most groundwater in Santa Clara County as potential drinking water. Therefore, Federal and State Maximum Contaminant Levels (MCLs) for drinking water must be proposed as the numerical objective (water quality objective). However, as of September 1998, MCLs for MTBE (and other ether oxygenates) have not been established. A secondary (aesthetic) MCL of 5 ppb for MTBE has been proposed by the Department of Health Services (DHS). In addition, by June 1999 a primary MCL must be established by the DHS. The lower of either MCL (once final) must be considered the water quality objective.

Final cleanup levels will generally be based on the drinking water MCL, and therefore, may be as low as 5 ppb for MTBE.

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What about cleanup levels for other petroleum hydrocarbons?

23 CCR, Section 2721 applies to typical petroleum hydrocarbons as well as recalcitrant compounds. However, in cases where petroleum hydrocarbon plumes are adequately defined and shown to be low risk, natural attenuation can be proposed to cleanup the contaminants to applicable water quality objectives. In some cases, for example with benzene, a case can be closed prior to achieving the 1 ppb water quality objective (MCL for benzene) if natural attenuation processes will degrade the contaminants in a reasonable amount of time. However, since natural attenuation mechanisms cannot be relied upon with recalcitrant chemicals, the water quality

objective must be met prior to closure.

What if the water quality objective cannot be achieved?

If interim and final cleanup efforts are conducted and it is determined that cleanup to water quality objectives is technologically infeasible, residual risk management requirements can be considered. However, residual risk management will only be considered as a last resort to protecting groundwater supplies. Please refer to page 9 of "Guide to Satisfying Regulatory Requirements and Protecting Groundwater" for additional information regarding residual risk management plans.

1. A 200 ppb Tier 1 level for investigation was developed from the Domenico 1987 solution for steady-state contaminant transport in which the model predicted that 200 ppb in the source area is considered to be protective of receptors at distances greater than 2000 feet - as presented in a tiered risk based decision making approach presented by Mr. Ravi Arulanantham of the SFRWQCB as interim guidance for MTBE sites